

THERMAL BEHAVIOUR OF WOODY BIOMASS AND ITS RELEVANCE TO COAL THERMOPLASTICITY

N. SMATANOVÁ¹, A.G. BORREGO² & M.A. DIEZ³

¹Institute of Combined Studies in Most, Faculty of Mining and Geology, VŠB – Technical University of Ostrava, Czech Republic

^{2,3}Instituto Nacional del Carbón, INCAR-CSIC, Francisco Pintado Oviedo, Spain

ABSTRACT

Sustainable biomass in modern blast furnaces has given rise to an environmentally friendly option for reducing CO₂ emissions and the use of fossil fuels. In the steel industry, biomass is also seen as a potential additive to coal blends in the production of coke used to feed blast furnaces. Within this framework, the present study aims to shed light on the effect of several woody biomasses on the thermoplastic properties of coking coals, due to the relevance of thermoplasticity to the development of the structure of coke and, consequently, to its physical and chemical behaviour in a blast furnace. As the ratio of the three main components in a biomass (cellulose, hemicellulose and lignin) differs with the source of the biomass in quantity and thermal behaviour, model biopolymers were also studied. An attempt was then made to explain the different degrees of reduction of thermoplasticity in a medium-fluid coal as being due to the type of wood species and to relate it to the thermal behaviour of the model lignocellulosic polymers. Multiple linear regression analysis was applied to a set of woody biomasses with different thermogravimetric patterns and composition in order to assess the contribution of the quantity and source of the volatiles evolved during pyrolysis to the fluidity of blends of coal and biomass.

KEYWORDS: Biomass, Biopolymers, Coking Coal, Fluidity, Thermogravimetry, Volatile Evolution

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INTRODUCTION

The partial substitution of fossil fuels for biomass in thermochemical processes has become an industrially attractive option, because its use may constitute an environmentally friendly action for reducing fossil CO₂ emissions in the short term and for achieving a sustainable CO₂ atmospheric concentration. Within this framework, woody biomass is seen in the steel industry as a viable source for reducing agent in blast furnaces [1-5], and as an additive to coal blends for the production of coke to feed blast furnaces [6-11]. Given the relevance of the thermoplastic properties of coal for the development of the structure and properties of coke, the effect of the addition of biomass on the thermoplastic properties of coal has been previously investigated [7,10,11]. It has been reported that biomass, even when added to low concentrations, leads to a reduction in maximum fluidity as determined by Gieselerplastometry [7,10] and high-temperature small-amplitude oscillatory shear (SAOS) rheometry [11]. Additionally, the use of commercially available model biopolymers and tars obtained from *Eucalyptus* wood have shown that the effect of biomass is strongly dependent on the relative amount of its woody constituents -hemicellulose, cellulose and lignin- [7,10]. As the ratio of the three components in a woody biomass differs from one wood species to another, the aim of the present work is to discuss the differences in the thermal

behaviour and composition of different wood species and their effects on the development of the fluidity of a coking coal. Thermogravimetric analysis will be used for providing rapid quantification and information about the source and thermal events of volatiles from several biomass and model biopolymers. The fluidity of blends made up of a coking coal and biomass at an addition rate of 2 wt% will be assessed by using Gieselerplastometry.

EXPERIMENTAL

Raw Materials

Twelve woody biomasses from the forestry sector and fruit tree pruning, which belong to different species and botanic families were selected (Table 1) together with six commercial woody polymers from Sigma Aldrich which were chosen as model compounds: two types of cellulose in the form of a powder with an average particle size of 20 μm (Cel) and long fibers (Cel2); two archetypal xylans, the most commonly used representative biopolymer of hemicellulose, -one from oat spelts with a particle size <600 μm (Xyl) and another from beech wood with a particle size <212 μm (Xyl2); and two alkali lignins in powder form with a particle size <212 μm and an average molecular weight of 28 kDa (Lig) and 10 kDa (Lig2).

Table 1: Selected woody biomass

Woody Biomass	Specie	Family
Alder	<i>Alnus glutinosa</i>	Betulaceae
Apple	<i>Malus domestica</i>	Rosaceae
Ash	<i>Fraxinus excelsior</i>	Oleaceae
Birch	<i>Betula celtiberica</i>	Betulaceae
Black Acacia	<i>Acacia melanoxylon</i>	Fabaceae
Brown	<i>Castanea sativa</i>	Fagaceae
Eucalyptus	<i>Eucalyptus globulus</i>	Myrtaceae
Maple	<i>Acer pseudoplatanus</i>	Sapindaceae
Olive	<i>Olive europaea</i>	Oleaceae
Pine	<i>Pinus radiata</i>	Pinaceae
Oak	<i>Quercus rubra</i>	Fagaceae
	<i>Quercus robur</i>	

A coking coal B from Bowen Basin (Queensland, Australia) was selected for blending with woody biomass and model wood constituents at an addition rate of 2 wt%. This coal is characterized by a relatively high Gieseler fluidity (1842 ddpm), a volatile matter content of 25 wt% dry basis and is able to produce a metallurgical coke with a high mechanical strength and a low reactivity to CO_2 .

Thermogravimetric Analysis

Pyrolysis experiments were carried out using a TG/DSC1 Mettler Toledo thermoanalyzer. Samples of about 6 mg with a particle size of <212 μm were heated from ambient temperature up to 1000 $^{\circ}\text{C}$ at a rate of 20 $^{\circ}\text{C}/\text{min}$ and the final temperature was held for 5 min. Nitrogen as an inert and sweep gas was supplied at a flow rate of 75 ml/min.

Gieselerplastometry

The thermoplastic characteristics of the coals and their blends with biomass were determined by using a R.B. Automazione Gieselerplastometer PL2000, according to ASTM D2639 and ISO 10329 Standards. Briefly, compacted samples (5 g, <0.425 mm) were heated up to 500 $^{\circ}\text{C}$ at a heating rate of 3 $^{\circ}\text{C}/\text{min}$ in the absence of air. The rotation of a stirrer placed inside the sample indicated the fluidity which was recorded in dial divisions per minute (ddpm) as a function

of the temperature. The maximum fluidity value (Fmax) and the temperature reached at this point (Tf) were recorded together with the softening and resolidification temperatures (Ts and Tr, respectively). The plastic or fluid interval was estimated by the difference between Tr and Ts. Fmax and the plastic interval are the key thermoplastic or rheological parameters used by the coking industry to evaluate the coals and additives for cokemaking and to formulate complex blends.

RESULTS AND DISCUSSIONS

Thermogravimetric Analysis of Model Woody Biopolymers and Wood Species

Figure 1 displays the thermal degradation profiles of the structural cell-wall polymers of wood, showing that each polymer behaves distinctly during pyrolysis. Xylan-type hemicellulose and lignin are less thermally stable than cellulose. They start to decompose at nearly 200 °C after the removal of physically adsorbed water, while the degradation of cellulose begins at around 300 °C. The mass loss rate (DTG) of cellulose occurs in a narrow temperature interval of nearly 100 °C and it is reflected as a sharp peak with a maximum value of 50 %/min at 354 and 368 °C for Cel and Cel2, respectively. Qualitatively there is a close similarity between the degradation of xylan from oat spelts (Xyl) and cellulose, while that of xylan from beech wood (Xyl2) has a different DTG profile. The gas evolution of Xyl takes place in a temperature interval of 75 °C and DTGmax is in the order of 60 %/min. However, the degradation of xylan from beech (Xyl2) shows two overlapping peaks of similar intensity (DTGmax, 11.4 and 12.1 %/min), five times lower than those of cellulose and Xyl, the temperature gap between the two peaks being around 50 °C. Unlike to the structural skeleton of cellulose, -which is a linear homopolymer composed of D-glucose units linked by $\beta(1\rightarrow4)$ glycosidic bonds and with an arrangement in which hydroxyl groups generate strong intra- and inter-molecular hydrogen bonds-, hemicellulose and its archetypal xylan is a complex, branched and heterogeneous polymeric network of different polysaccharides, based on pentoses such as xylose and arabinose, hexoses such as glucose, mannose and galactose, and sugar acids. The differences in structure are reflected in the different pyrolytic behaviour observed in xylans, caused by cleavage of the glycosidic groups at low temperatures. At about 400 °C, the degradation of the molecular structure of hemicellulose and cellulose is totally complete. Cellulose is mainly a precursor of gas and liquid products with a small amount of solid after pyrolysis (12 and 5% for Cel and Cel2, respectively), while xylan also contributes to the formation of solid product (28 and 20% for Xyl and Xyl2, respectively).

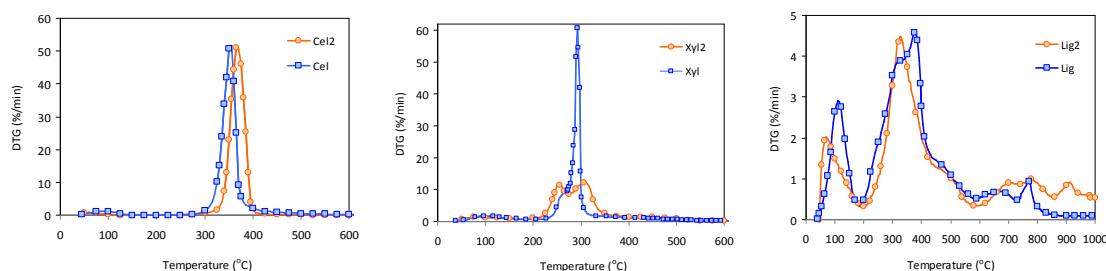


Figure 1: DTG Profiles of Model Biopolymers, Xylan, Cellulose and Lignin

A different thermal history is observed for lignin. Lignin is a polyphenolic polymer with a 3D macromolecular structure binding the cells, fibres and vessels. Its heterogeneous, cross-linked and branched molecular network varies from one species to another. Although lignin is less thermally stable than cellulose, the thermal breakdown of the complex lignin structure does not occur over a narrow range of pyrolysis temperatures. The pyrolysis process is very slow and spread out

over a wide temperature interval from 200 °C up to 900-1000 °C in different overlapping stages. The char left over from lignin pyrolysis (approx. 45%) was the highest. The temperature gap between the main peaks of the two lignins (54 °C) is consistent with their different molecular weight, 28 kDa for Ligvs. 10 kDa for Lig2.

Wood pyrolysis is considered to be a simultaneous and continuous degradation of the three major constituents, hemicelluloses, cellulose and lignin. As an example, Figure 2 shows the DTG profiles of five different wood species.

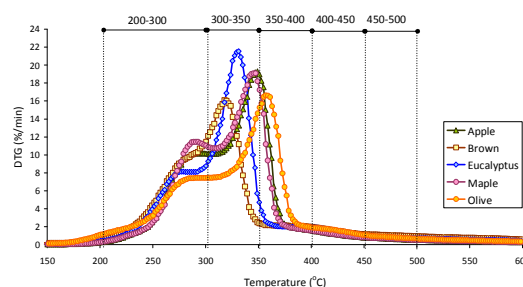


Figure 2: TG and DTG Profiles of Five Different Wood Species

The first point to note in the DTG profiles is that the decomposition of the woods tested can occur at slightly different temperatures as a consequence of the amount of volatile matter evolved from each constituent, its macromolecular structure, chemical interactions between the biopolymers and catalytic effects of the inorganic matter. As previously stated for single wood constituents, hemicellulose degrades first, its profile overlapping that of cellulose (shoulder at low temperature) while at the same time the partial degradation of the more labile bonds occurs within the lignin structure. The extent of overlapping depends on the composition of the wood species. Thus, the major DTG peak could be related to the degradation of cellulose as the major component in wood and the major source of volatile products (oil and gases). Due to the complex composition of wood species, the overlapping between the release of volatile matter from the wood constituents and the temperature shifts of the maximum mass loss rate, several temperature intervals can be defined which are associated with the devolatilization of the main constituents (Figure 2). Thus, the DTG profiles of woody biomass can be regarded as a sum of pseudo-components in terms of decomposition products from hemicellulose, cellulose and lignin with a similar thermal stability, but different relative proportions of wood components. Pseudo-components can be considered to be correlated with other properties of biomass and their blends with coal such as thermoplasticity.

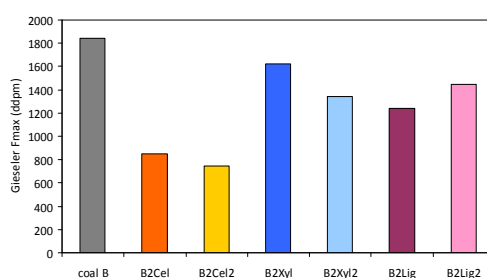
Effect of Model Biopolymers and Wood Species on Coal Rheological Properties

When certain coals are heated in an oxygen-deficient atmosphere at high temperature for an adequate period of time, a dense, strong and more or less graphitic-ordered carbon (*called coke*) is produced together with liquid and gaseous chemicals as by-products. The thermoplastic properties of coal in the temperature range 350-500 °C determine the type of coal that is suitable for producing a high-quality coke. While volatile products are evolved, the coal particles soften to various degrees, decompose sufficiently to become fluid, change volume and then bond together, resolidifying into a semicoke (*intermediate carbon material in the coal-to-coke transformation*). This transient stage of coal -plastic or fluid stage- is important not only during the carbonization of bituminous coals where this property is absolutely indispensable to the formation of metallurgical coke, but also it is relevant in combustion, gasification and other conversion processes of coal. Thus, a basic knowledge and control of such coal properties is necessary to improve conversion processes and optimize feedstocks. The most widely used method for measuring coal plasticity/fluidity is the rotational viscosimeter designed by Gieseler.

Additions of 2 wt% of model polymers produce a reduction in the Gieseler maximum fluidity (Fmax) of coking coal B from 1842 to 750 ddpm (Figure 3), with no significant change in the characteristic temperatures: (i) the softening temperature at which the coal first begins to flow with a fluidity of 1.0 ddpm (397-402 °C); (ii) the temperature at which the fluid mass resolidifies into semicoke (493-496 °C); (iii) the temperature at which maximum fluidity is achieved (456-459 °C); and the plastic range of about 96 °C. As previously reported for a low-fluid coal (389 ddpm), cellulose is the strongest modifier of coal fluidity, while lignin and xylan have the less pronounced effect [10]. It appears therefore that it is the type of xylan and lignin that influences slightly the development of coal fluidity.

When wood is added to coal, it produces a decrease in the fluidity of between 35.5 and 48.2%. Although the fluidity of the blends with each wood occurs in a very narrow range from 955 to 1188 ddpm, certain differences and similarities can be established. *Eucalyptus*, *Pine* and *Olive* influence the development of coal fluidity to a similar extent. They produce the largest decrease which accounts for a loss of about 48%. *Black Acacia*, *Ash* and *Maple* also share similarity in that there is a decrease in coal fluidity between 35-37%, while the reduction in Fmax for the remaining woods occurs between 39 and 42%. If the model compounds are compared, the extent of the decrease in Fmax in these coal+biomass blends can be represented as follows: cellulose > woods > lignin \geq xylan.

The evolution of volatile products in gaseous form for a carbon feedstock and/or a carbon-source additive is considered a critical stage in the mechanism of carbonization and this phenomenon is associated to the effects on fluidity development [12-15]. In other words, the effectiveness of a feedstock or additive to modify a co-carbonization system can be related to the quantity and composition of volatiles released by the additive as well as the stage at which they are released (*before, during and after the coal plastic stage*). Such a relation has been clearly established by assessing the distribution of volatiles evolved at different temperature intervals by means of thermogravimetric analysis. The volatile matter evolved between 400 and 500 °C is seen as a critical parameter for assessing the potential effect of carbon additives such as petroleum cokes [12], bituminous chemicals [14] and plastic wastes [15] on coal thermoplasticity. From previous studies, it is shown that if the release of volatiles occurs too early, before the feedstock become fluid, they leave the co-carbonization system without making any significant contribution to fluidity development [13]. This is the case of xylan-type hemicellulose where most of the volatiles are evolved below 300 °C (Figure 4).



**Figure 3: Variation of Gieseler Maximum Fluidity
Addition of 2 wt% of Model Biopolymers**

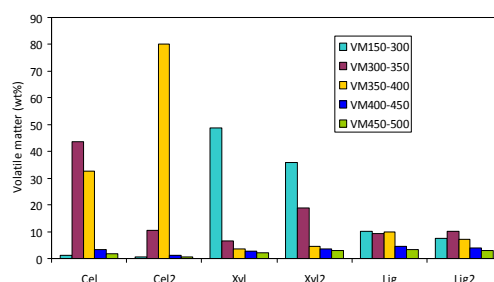


Figure 4: Distribution of Volatile Products Evolved During Pyrolysis of Model Biopolymers

Lignin may play a double role, because it decomposes over a wide temperature range affecting the entire stage of coal fluidity development. Cellulose seems to be a more active agent in destroying the coal fluid components near the onset of softening. However, the amount of volatile matter generated by biopolymers and wood species in the critical temperature range of coal development is very small (4-6 wt%), even at a relatively rapid heating rate of 20 °C/min, while below 400 °C it accounts for 60-75 wt%. Consequently, other factors must contribute to the significant reduction in coal fluidity when coal is blended with only 2 wt% biomass. Indeed, most of the volatiles generated during pyrolysis are linked to highly oxygenated species in the permanent gases (CO₂ and CO together with H₂, CH₄, C_xH_y) and condensable chemicals such as acetic acid, methanol, acetone, furfural, levoglucosane and methoxyphenol derivatives which constitute bio-oil or tar. The progressive removal of oxygenated-compounds in the earliest stages of coal carbonization could lead to structural instability in coal before it becomes fluid and prevent coal particles from fusing and agglomerating.

Within this framework, at stages close to the onset temperature of coal softening the generation and composition of volatiles makes a significant contribution to reducing the fluidity of the reaction system. Thermogravimetric data obtained from the model biopolymers and several wood species illustrate the generation of volatiles at different thermal events (Figures 1-3) and could provide information about their quantity and wood-source. Such considerations led us to investigate the way in which the amount of evolved gases at different pyrolysis steps affects coal fluidity by using a very simple approach based on linear regression analysis.

Firstly, a number of linear regression analysis were tested, using the volatile matter evolved in each of the five thermal events of wood and biopolymers (Figure 2) as a dependent variable. Due to the poor correlation between fluidity and each of these variables (correlation coefficients $r < 0.8$), multiple linear regression analysis was performed. Collinearity was dealt with at two levels: (1) variables with high correlation coefficients were segregated and such variables were used in separate regressions, but not in the same regressions; and (2) a regression was accepted only if the standard error was low and the correlation coefficient relatively high. MLR is an improvement on the simple linear model, including only one variable. As an example, the following MLR equation with correlation coefficient of 0.920 was applied to a group of blends of coal and woody biomass with different thermogravimetric patterns and, then, different compositions.

$$F_{\max} = 1842 + (1.56 \text{ VM}_{200-300}) - (9.50 \text{ VM}_{300-350}) - (10.52 \text{ VM}_{350-400}) - (93.61 \text{ VM}_{400-450})$$

In all cases, the experimental and estimated F_{\max} values differ in less than 120 ddpm.

CONCLUSIONS

Comparative studies of different wood species show that small variations in the development of coal fluidity are

associated with the different compositions of the wood species. Volatile products released in different quantities and at different stages are dependent on the wood species. A complex chemical phenomenon induced by the high oxygen-functionalized volatile compounds generated during biomass pyrolysis causes a decrease in the fluidity of coal. At the same time, they can promote a devolatilization of the light compounds derived from the decomposition of coal and instability in coal structure which are the factors responsible for initiating coal softening. Although the differences in fluidity of the blends are small they are significant enough to suggest that the quantity and the source of volatiles is a critical factor in the reduction of fluidity. A mathematical model based on multiple linear regression was developed to reflect the effect of biomass constituents on the development of coal fluidity.

REFERENCES

1. Birat, J.P. and Hanrot, F., *ULCOS-European Steelmakers' efforts to Reduce Greenhouse Gas Emissions, Proceedings of the 5th European Coke and Ironmaking Congress, Stockholm, Sweden, 2005.*
2. Ariyama, T. and Sato, M., 2006. *Optimization of Ironmaking Process for Reducing CO₂ Emissions in the Integrated Steel Works, ISIJ International* 46(12) 1736-1744.
3. Hanrot, F., Sert, D., Delinchant, J., Pietruck, R., Bürgler, T., Babich, A., Fernández, M., Alvarez, R. and Diez, M.A. 2009. *CO₂ Mitigation for Steelmaking using Charcoal and Plastics Wastes as Reducing Agents and Secondary Raw Materials. Proceedings of the 1st Spanish National Conference on Advances in Materials Recycling and Eco-Energy. Recimat09, Madrid, Spain, 2009. Available at: <http://hdl.handle.net/10261/18433>.*
4. Babich, A., Ohno, K., Senk, D., Gudenau, H.W., Kowitwarangkul, P., Ueki, Y. and Shimizu, M., *Use of Charcoal, Biomass and Waste Plastics for Reducing CO₂ Emission in Ironmaking, Proceedings of the 6th European Coke and Ironmaking Congress. METEC InSteel Con'2011, CD-Format, Düsseldorf, Germany, 2011.*
5. Norgate, T., Haque, N., Somerville, M. and Jahanshahi, S. 2012. *Biomass as a Source of Renewable Carbon for Iron and Steelmaking. ISIJ International* 52 (8), 1472-1481.
6. Sakurovs, R. 2000. *Some Factors Controlling the Thermoplastic Behaviour of Coals, Fuel* 79, 379-389.
7. Diez, M.A., Alvarez, R., Fernández, M., *Biomass Derived Products as Modifiers of the Rheological Properties of Coking Coals. Proceeding of the 1st Spanish National Conference on Advances in Materials Recycling and Eco-Energy. Recimat09. Madrid, Spain, 2009. Available at: <http://hdl.handle.net/10261/18359>.*
8. MacPhee, J.A., Gransden, J.F., Giroux, L. and Price, J.T. 2009. *Possible CO₂ mitigation via addition charcoal to coking coal blends. Fuel Processing Technology* 90, 16-20.
9. Thomas, S., McKnight, S.J., Serrano, E.J., Maslejova, A., Zelinsky, R., Tomás, J., Vlastic, P., *Laboratory Evaluation of Biomass Usage for Coke and Sinter Production. METEC InSteel 2011, CD-format, Düsseldorf, Germany, 2011.*
10. Diez, M. A., Alvarez, R., Fernández, M. 2012. *Biomass Derived Products as Modifiers of the Rheological Properties of Coking Coals, Fuel* 96, 306-313.
11. Castro Díaz, M., Zhao, H., Kokonya, S., Dufour, A., Snape, C.E. 2012. *The Effect of Biomass on Fluidity Development in Coking Blends Using High-Temperature SAOS Rheometry, Energy & Fuels* 26 (3), 1767-1775.
12. Menéndez, J. A., Pis, J. J., Alvarez, R., Barriocanal, C., Fuente E. and Diez, M.A. 1996. *Characterization of Petroleum Coke as an Additive in Metallurgical Cokemaking. Modification of Thermoplastic Properties of Coal, Energy & Fuels* 10, 1262-1268.
13. Rodríguez-Reinoso, F., Santana, P., Romero-Palazón, E., Diez, M.A. and Marsh, H. 1998. *Delayed Coking: Industrial and*

Laboratory Aspects, Carbon 36(1), 105-116.

14. Diez, M.A., Domínguez, A., Barriocanal, C., Alvarez, R., Blanco, C.G., Casal, M.D. and Canga, C.S. 1998. Gas chromatographic study for the evaluation of the suitability of bituminous waste material as an additive for coke production, *Journal of Chromatography A* 823, 527–536.
15. Diez, M.A., Barriocanal, C. and Alvarez, R. 2005. Plastic Wastes as Modifiers of the Thermoplasticity of Coal, *Energy & Fuels* 19, 2304-2316.

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